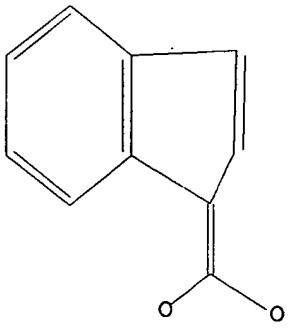
=>
Uploading C:\Program Files\Stnexp\Queries\735a.str

L6 STRUCTURE UPLOADED

=> d l6
L6 HAS NO ANSWERS
L6 STR



Structure attributes must be viewed using STN Express query preparation.

=> s l6
REGIstRY INITIATED
Substance data SEARCH and crossover from CAS REGISTRY in progress...
Use DISPLAY HITSTR (or FHITSTR) to directly view retrieved structures.

SAMPLE SEARCH INITIATED 14:16:34 FILE 'REGISTRY'
SAMPLE SCREEN SEARCH COMPLETED - 3869 TO ITERATE

51.7% PROCESSED 2000 ITERATIONS 3 ANSWERS
INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)
SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE **COMPLETE**
BATCH **COMPLETE**
PROJECTED ITERATIONS: 73650 TO 81110
PROJECTED ANSWERS: 3 TO 260

L7 3 SEA SSS SAM L6

L8 2 L7

=> d 1-2 ibib abs hitstrr
'HITSTRR' IS NOT A VALID FORMAT FOR FILE 'CAPLUS'

The following are valid formats:

ABS --------- GI and AB
ALL --------- BIB, AB, IND, RE
APPS -------- AI, PRAI
BIB --------- AN, plus Bibliographic Data and PI table (default)
CAN --------- List of CA abstract numbers without answer numbers
CBIB -------- AN, plus Compressed Bibliographic Data
DALL -------- ALL, delimited (end of each field identified)
DMAX -------- MAX, delimited for post-processing
FAM --------- AN, PI and PRAI in table, plus Patent Family data

FBIB -------- AN, BIB, plus Patent FAM
IND --------- Indexing data
IPC --------- International Patent Classifications
MAX --------- ALL, plus Patent FAM, RE
PATS -------- PI, SO
SAM --------- CC, SX, TI, ST, IT
SCAN -------- CC, SX, TI, ST, IT (random display, no answer numbers;
SCAN must be entered on the same line as the DISPLAY,
e.g., D SCAN or DISPLAY SCAN)
STD --------- BIB, IPC, and NCL

IABS -------- ABS, indented with text labels
IALL -------- ALL, indented with text labels
IBIB -------- BIB, indented with text labels
IMAX -------- MAX, indented with text labels
ISTD -------- STD, indented with text labels

OBIB -------- AN, plus Bibliographic Data (original)
OIBIB ------- OBIB, indented with text labels

SBIB -------- BIB, no citations
SIBIB ------- IBIB, no citations

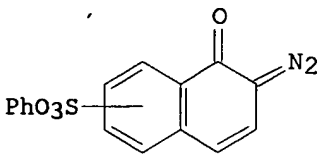
HIT --------- Fields containing hit terms
HITIND ------ IC, ICA, ICI, NCL, CC and index field (ST and IT)
containing hit terms
HITRN ------- HIT RN and its text modification
HITSTR ------ HIT RN, its text modification, its CA index name, and
its structure diagram
HITSEQ ------ HIT RN, its text modification, its CA index name, its
structure diagram, plus NTE and SEQ fields
FHITSTR ----- First HIT RN, its text modification, its CA index name, and
its structure diagram
FHITSEQ ----- First HIT RN, its text modification, its CA index name, its
structure diagram, plus NTE and SEQ fields
KWIC -------- Hit term plus 20 words on either side
OCC --------- Number of occurrence of hit term and field in which it occurs

To display a particular field or fields, enter the display field codes. For a list of the display field codes, enter HELP DFIELDS at an arrow prompt (=>). Examples of formats include: TI; TI,AU; BIB,ST; TI,IND; TI,SO. You may specify the format fields in any order and the information will be displayed in the same order as the format specification.

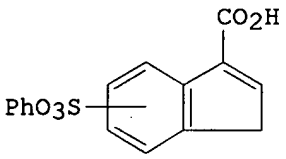
All of the formats (except for SAM, SCAN, HIT, HITIND, HITRN, HITSTR, FHITSTR, HITSEQ, FHITSEQ, KWIC, and OCC) may be used with DISPLAY ACC to view a specified Accession Number.
ENTER DISPLAY FORMAT (BIB):end

=> d 1-2 ibib abs hitstr

L8 ANSWER 1 OF 2 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1993:38553 CAPLUS
DOCUMENT NUMBER: 118:38553
TITLE: Synthesis and photochemistry of 1,2-naphthoquinonediazide-(2)-n-sulfonic acid derivatives
AUTHOR(S): Bendig, J.; Sauer, E.; Polz, K.; Schopf, G.
CORPORATE SOURCE: Inst. Org. Chem., Humboldt Univ., Berlin, 0-1040, Germany
SOURCE: Tetrahedron (1992), 48(42), 9207-16
CODEN: TETRAB; ISSN: 0040-4020
DOCUMENT TYPE: Journal
LANGUAGE: English
GI



I



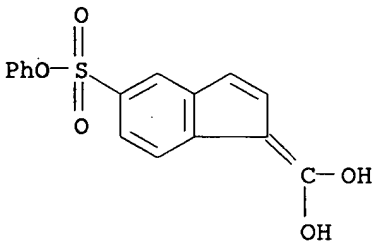
II

AB The 1,2-naphthoquinonediazide-(2)-6- and -7-sulfonic acid esters I (sulfonyl position = 7, 8) were synthesized for the first time starting from the corresponding 1-naphthylamine-6- and -7-sulfonic acids, resp., via Bucherer reaction, nitrosation, reduction, diazotation, sulfochlorination, esterification. The synthesis of the corresponding 8-sulfonic acid ester was not successful by this way. On photolysis, I form the corresponding (phenoxysulfonyl)indenecarboxylic acids II in the same manner like the known 5-sulfonic acid derivative On the other hand, photolysis of the 4-sulfonic acid ester photochem. induced ester cleavage occurs addnl. (λ <320 nm).

IT **145074-73-3P**
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and rearrangement of)

RN 145074-73-3 CAPLUS

CN 1H-Indene-5-sulfonic acid, 1-(dihydroxymethylene)-, phenyl ester (9CI) (CA INDEX NAME)



L8 ANSWER 2 OF 2 CAPLUS COPYRIGHT 2005 ACS on STN

ACCESSION NUMBER: 1988:437562 CAPLUS

DOCUMENT NUMBER: 109:37562

TITLE: Electrophilic substitution of benzofulvenes with activated sulfoxides

AUTHOR(S): Teuber, Dorothee; Hartke, Klaus

CORPORATE SOURCE: Inst. Pharm. Chem., Univ. Marburg, Marburg, D-3550, Fed. Rep. Ger.

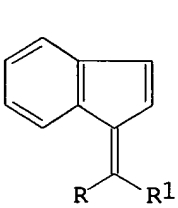
SOURCE: Liebigs Annalen der Chemie (1988), (1), 39-42
CODEN: LACHDL; ISSN: 0170-2041

DOCUMENT TYPE: Journal

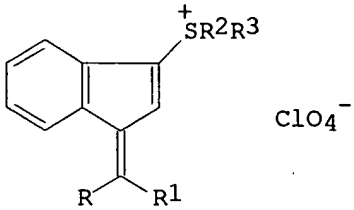
LANGUAGE: German

OTHER SOURCE(S): CASREACT 109:37562

GI



I



II

AB The benzofulvenes I (R = R1 = Ph, Me, EtO, MeS; R = Me, R1 = Ph) were treated with R2R3SO [R2 = R3 = Me, PhCH2, Ph, p-MeC6H4; R2 = R3 = (CH2)4, CH2CH2OCH2CH2] in presence of (F3CCO)2O followed by aqueous LiClO4 to give the sulfoniobenzofulvene perchlorates II.

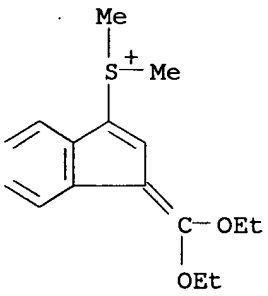
IT **115176-52-8P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)

RN 115176-52-8 CAPLUS

CN Sulfonium, [1-(diethoxymethylene)-1H-inden-3-yl]dimethyl-, perchlorate (9CI) (CA INDEX NAME)

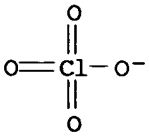
CM 1

CRN 115176-51-7
CMF C16 H21 O2 S



CM 2

CRN 14797-73-0
CMF Cl O4



=> s l6 full
REGISTRY INITIATED
Substance data SEARCH and crossover from CAS REGISTRY in progress...
Use DISPLAY HITSTR (or FHITSTR) to directly view retrieved structures.

FULL SEARCH INITIATED 14:17:58 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED - 77168 TO ITERATE

100.0% PROCESSED 77168 ITERATIONS 39 ANSWERS
SEARCH TIME: 00.00.01

L9 39 SEA SSS FUL L6

L10 23 L9

=> s l10 and py<2002

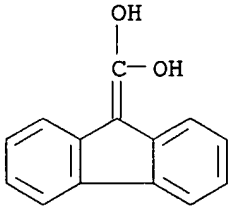
21804242 PY<2002
L11 21 L10 AND PY<2002

=> d 1-10 ibib abs hitstr

L11 ANSWER 1 OF 21 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 2000:667072 CAPLUS
DOCUMENT NUMBER: 133:334870
TITLE: Calculated pKEnol Values for β,β-Diarylacetic Acids and β,β-Diarylacetaldehydes. Effect of Steric Bulk of Substituents on the Relative Stability of Enols of Carboxylic Acids and Aldehydes
AUTHOR(S): Yamataka, Hiroshi; Rappoport, Zvi
CORPORATE SOURCE: Institute of Scientific and Industrial Research, Osaka University, Ibaraki Osaka, 567-0047, Japan
SOURCE: Journal of the American Chemical Society (**2000**), 122(40), 9818-9828
CODEN: JACSAT; ISSN: 0002-7863
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English

AB The energies, pKEnol values, structures, and conformations of vinyl alc. (3a), acetaldehyde (4a), 1,1-ethenediol (5a), acetic acid (6a), and six derivs. of each substituted by two β-aryl groups of increasing bulk from Ph to Tip (2,4,6-tri-i-PrC6H2) were calculated by the B3LYP method in order to evaluate quant. the pKEnol reducing effect of bulky aryl groups. Also calculated were the same parameters for the ArCHXCO2H/ArC(X):C(OH)2 pairs for Ar = Ph, X = CN (9a/9b), OH (10a/10b), for which pKEnol is known, and for Ar = Mes (mesityl), X = CN. All the substituents significantly decrease the pKEnol values from 22.4 (6a/5a) and 9.1 (4a/3a). For example, pKEnol = 0.2, -2.7, -2.0, and -2.7 for ArAr'CHCHO/ArAr'C:CHOH and 13.3, 11.5, 9.2, and 9.3 for ArAr'CHCO2H/ArAr'C:C(OH)2 when Ar,Ar' = Ph,Ph, Ph,Mes, Mes,Mes, and Tip,Tip, resp. For 9a/9b and 10a/10b, the calculated pKEnol values resemble the observed ones. The enols and enediols (except 3b and 5b, when Ar2C: = fluorenylidene) have a propeller conformation. The Ar-C:C torsional angles increase with increasing bulk of the aryl group, but for Ph,bulkier Ar the Ar-C:C torsional angle strongly exceeds the Ph-C:C angle. The syn-C:C-O-H conformer is preferred over the anti conformer for all the enols 3. For the 1,1-enediols, the syn,syn conformer is preferred for most Ar,Ar' combinations, but the syn,anti conformer is preferred for 5a and 5h [ArAr'C=C(OH)2; Ar = Ph, Ar' = 2,4,6-(t-Bu)3C6H2], and 10a, and the anti,anti conformation is the least stable. The stabilization and conformational preferences were analyzed both qual. and with the aid of appropriate isodesmic reactions. Superposition of stabilizing Ar-C:C conjugation effects, stabilization of the carbonyl forms, and π(Ar)···O hydrogen bonding and destabilizing geminal Ar/Ar' and vicinal cis-Ar/OH steric interactions account for the results. The low enol or enediol content is mainly due to the relative stabilization of the aldehyde or acid form, and the β-Ar groups stabilize the enols mainly by conformation-dependent Ar-C:C conjugation and π(Ar)···HO H-bonding.

IT **263709-40-6**
RL: PRP (Properties)
(ab initio study of relative stability of enols of carboxylic acids and aldehydes)
RN 263709-40-6 CAPLUS
CN Methanediol, 9H-fluoren-9-ylidene- (9CI) (CA INDEX NAME)



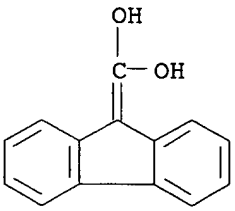
REFERENCE COUNT: 62 THERE ARE 62 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 2 OF 21 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 2000:74486 CAPLUS
DOCUMENT NUMBER: 132:278887
TITLE: Simultaneous pH-rate profiles applied to the two step consecutive sequence A → B → C : a theoretical analysis and experimental verification
AUTHOR(S): Andraos, John; Lathioor, Edward C.; Leigh, William J.
CORPORATE SOURCE: Department of Chemistry, University of Toronto, Toronto, ON, M5S 3H6, Can.
SOURCE: Perkin 2 (**2000**), (2), 365-373
CODEN: PRKTFO
PUBLISHER: Royal Society of Chemistry
DOCUMENT TYPE: Journal
LANGUAGE: English

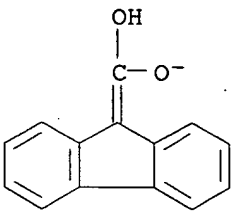
AB The absorbance extremum method introduced to resolve the rate constant-reaction step ambiguity problem in 2 step consecutive reactions is applied to cases where the rate constant in each step is pseudo 1st order and dependent on catalyst concentration In particular, acid and base catalyzed reactions of substrates in aqueous solution are examined Resultant simultaneous pH-rate profile functions are treated in the context of the ambiguity problem and a detailed account of the possible interactions between pH-rate profiles is also given. The merits of this method include its general scope, its applicability to reactions for which it may be exptl. difficult to resolve the ambiguity assignment by other means, its use of rate data acquired from original kinetic traces without requiring addnl. information. The theor. anal. is verified and tested exptl. for the hydration of fluorenylideneketene in dilute aqueous HClO4 solns.

IT **263709-40-6 263709-41-7**
RL: FMU (Formation, unclassified); PEP (Physical, engineering or chemical process); PRP (Properties); RCT (Reactant); FORM (Formation, nonpreparative); PROC (Process); RACT (Reactant or reagent)
(mechanistic reaction intermediate; theor. anal. and exptl. verification of simultaneous pH-rate profiles applied to two step consecutive sequence A → B → C)

RN 263709-40-6 CAPLUS
CN Methanediol, 9H-fluoren-9-ylidene- (9CI) (CA INDEX NAME)



RN 263709-41-7 CAPLUS
CN Methanediol, 9H-fluoren-9-ylidene-, ion(1-) (9CI) (CA INDEX NAME)



REFERENCE COUNT: 17 THERE ARE 17 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

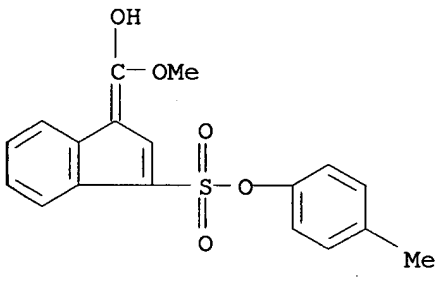
L11 ANSWER 3 OF 21 CAPLUS COPYRIGHT 2005 ACS on STN

ACCESSION NUMBER: 1995:262850 CAPLUS
DOCUMENT NUMBER: 122:105122
TITLE; Photodecomposition mechanism of o-diazonaphthoquinones studied by laser flash photolysis with infrared detection
AUTHOR(S): Oishi, Shigero; Watanabe, Yuriko; Kuriyama, Yasunao
CORPORATE SOURCE: Sch. Sci., Kitasato Univ., Kitasato, Sagamihara, Kanagawa, 228, Japan
SOURCE: Chemistry Letters (**1994**), (12), 2187-90
CODEN: CMLTAG; ISSN: 0366-7022
PUBLISHER: Nippon Kagakkai
DOCUMENT TYPE: Journal
LANGUAGE: English

AB Laser flash photolysis of an o-diazonaphthoquinone traced by monitoring IR in parallel with UV revealed the dynamic behavior of ketene intermediate, which appeared immediately after the laser pulse and changed swiftly to next intermediate. The fact that the conversion of ketene did not correspond to the formation of ketene hydrate suggested the existence of another intermediate between ketene and ketene hydrate.

IT **160815-99-6**
RL: FMU (Formation, unclassified); PEP (Physical, engineering or chemical process); RCT (Reactant); FORM (Formation, nonpreparative); PROC (Process); RACT (Reactant or reagent)
(mechanistic reaction intermediate; photodecompn. mechanism of o-diazonaphthoquinones studied by laser flash photolysis with IR detection)

RN 160815-99-6 CAPLUS
CN 1H-Indene-3-sulfonic acid, 1-(hydroxymethoxymethylene)-, 4-methylphenyl ester (9CI) (CA INDEX NAME)



L11 ANSWER 4 OF 21 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1995:40390 CAPLUS
DOCUMENT NUMBER: 122:68048
TITLE: Laser photolysis of naphthoquinone diazide in cyclohexane - two-laser chemistry
AUTHOR(S): Bendig, J.; Mitzner, R.
CORPORATE SOURCE: Inst. Organische Chemie, Humboldt-Univ., Berlin, D-10115, Germany
SOURCE: Berichte der Bunsen-Gesellschaft (**1994**), 98(8), 1004-8
CODEN: BBPCAX; ISSN: 0005-9021
DOCUMENT TYPE: Journal
LANGUAGE: English

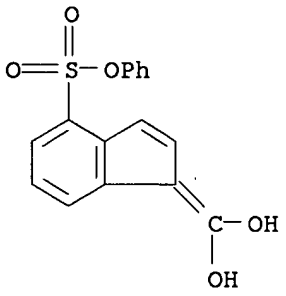
AB The laser photochem. of 1,2-naphthoquinone-diazide-(2)-5-sulfonic acid Ph ester in cyclohexane has been investigated. The photolysis expts. have been done using a KrF laser pulse (generation pulse) and a nitrogen laser pulse (transformation pulse) with various time delay from 40 ns up to 1 s. At a time delay between the two laser pulses in the μs-region, the formation of indene and cyclohexyl-indene derivs. has been observed, addnl. to the corresponding indenecarboxylic acid. The laser specific formation of these compds. is the result of the electronic excitation of the intermediately formed ketene and its reaction by decarbonylation. The time delay for getting a high yield of the indene and the

cyclohexyl-indene derivs. correlates closely with the rise time and the life time of the ketene.

IT **145074-72-2**
RL: FMU (Formation, unclassified); RCT (Reactant); FORM (Formation, nonpreparative); RACT (Reactant or reagent)
(transient; formation and photoreactions of transients in two-laser photolysis of naphthoquinone diazide in cyclohexane)

RN 145074-72-2 CAPLUS

CN 1H-Indene-4-sulfonic acid, 1-(dihydroxymethylene)-, phenyl ester (9CI) (CA INDEX NAME)



L11 ANSWER 5 OF 21 CAPLUS COPYRIGHT 2005 ACS on STN

ACCESSION NUMBER: 1994:190791 CAPLUS

DOCUMENT NUMBER: 120:190791

TITLE: Kinetics and Mechanism of the Isomerization of 1H-Indene-1-carboxylic Acid to 1H-Indene-3-carboxylic Acid in Aqueous Solution and Determination of Their Keto-Enol Equilibrium Constants and Acid Dissociation Constants of the Keto and Enol Forms. Implication for the Photolysis of Diazonaphthoquinones

AUTHOR(S): Andraos, J.; Kresge, A. J.; Popik, V. V.

CORPORATE SOURCE: Department of Chemistry, University of Toronto, Toronto, ON, M5S 1A1, Can.

SOURCE: Journal of the American Chemical Society (**1994**), 116(3), 961-7
CODEN: JACSAT; ISSN: 0002-7863

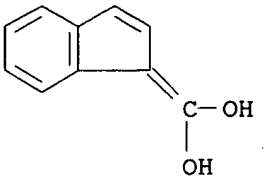
DOCUMENT TYPE: Journal

LANGUAGE: English

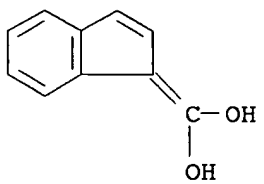
AB Rates of isomerization of 1H-indene-1-carboxylic acid to 1H-indene-3-carboxylic acid were measured in dilute aqueous solns. of HClO4, NaOH, and CH3CO2H and H2PO4-, (CH3)3CPO3H-, and HCO3- buffers. This gave a rate profile which, together with the occurrence of general base catalysis and sizable primary kinetic isotope effects, indicates that the isomerization takes place through an enolization-reketonization reaction sequence. The equilibrium constant of the isomerization reaction is K = [indene-3-carboxylic acid]/[indene-1-carboxylic acid] = 200 in aqueous acid solution and K = 100 in base. The ratio of products formed by ketonization of the indenecarboxylic acid enol intermediate generated in the photolysis of 2-diazo-1(2H)-naphthalenone is R = [indene-3-carboxylic acid]/[indene-1-carboxylic acid] = 0.47 in aqueous acid solution and R = 20 in base. The failure of previous investigations of the photolysis reaction to detect any indene-1-carboxylic acid as the product is attributed to the facile isomerization of this substance to indene-3-carboxylic acid and the preponderance of the latter at equilibrium The enol intermediate of this isomerization reaction was also generated by flash photolysis of 2-diazo-1(2H)-naphthalenone and rates of its ketonization were measured in dilute aqueous HClO4 solns. Anal. of the data gave the enol acidity constant pKaE = 2.09. The results, in combination with those for the isomerization reaction, also provided carbon acid acidity consts. (KaK) and keto-enol equilibrium consts. (KE) for the two acids: pKaK = 9.35 and pKE = 7.26 for indene-1-carboxylic acid and pKaK = 11.69 and pKE = 9.60 for indene-3-carboxylic acid.

IT **153470-52-1P**

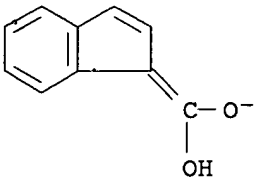
RL: RCT (Reactant); PREP (Preparation); RACT (Reactant or reagent)
(formation and tautomerization of)
RN 153470-52-1 CAPLUS
CN Methanediol, 1H-inden-1-ylidene- (9CI) (CA INDEX NAME)



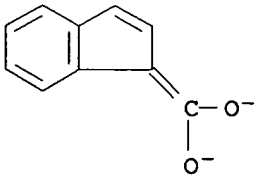
L11 ANSWER 6 OF 21 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1994:163330 CAPLUS
DOCUMENT NUMBER: 120:163330
TITLE: Flash Photolysis of α-Diazonaphthoquinones in Aqueous Solution: Determination of Rates and Equilibria for Keto-Enol Tautomerization of 1-Indene-3-carboxylic Acid
AUTHOR(S): Almstead, Ji In Kim; Urwyler, Bernhard; Wirz, Jakob
CORPORATE SOURCE: Institut fuer Physikalische Chemie, Universitaet Basel, Basel, CH-4056, Switz.
SOURCE: Journal of the American Chemical Society (**1994**), 116(3), 954-60
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: English
AB Flash photolysis of either 1-diazo-2(1H)-naphthalenone (1a) or 2-diazo-1(2H)-naphthalenone (1b) generates benzofulven-8-one (2). Hydrolysis of ketene 2 forms benzofulvene-8,8-diol (3), the enol tautomer of indene-3-carboxylic acid (4). PH rate profiles for the reactions 2 → 3 and 3 → 4 were determined in aqueous solution Ketonization of 3 is catalyzed by acid and by base. Catalysis by protons sats. in strongly acidic solns., thereby defining the first ionization constant of the enol, pKEa = 1.90 ± 0.05, catalysis by hydroxyl ions sats. in dilute base, defining the second ionization constant, pK'Ea = 8.3 ± 0.2. The first (OH) and second (CH) ionization consts. of 4 were determined by spectrophotometric titration, pKKa = 4.50 ± 0.03 and pK'Ka = 15.2 ± 0.2. Two independent ests. of the enolization consts. of 4 and 4-, the first based on thermodn. cycles, the second on the ratio of enolization and ketonization rates, were combined to give pKE = 9.3 ± 0.3, pK'E = 6.6 ± 0.3. Ketene 2 is formed by irradiation of 1-bromo-2-naphthol at 12 K in an argon matrix, but neither it nor its isomer 2-bromo-1-naphthol were suitable for the generation and observation of 2 and 3 by flash photolysis in aqueous solution
IT **153470-52-1 153470-53-2 153470-55-4**
RL: PRP (Properties)
(ionization consts. and tautomerization of indenecarboxylic acid)
RN 153470-52-1 CAPLUS
CN Methanediol, 1H-inden-1-ylidene- (9CI) (CA INDEX NAME)



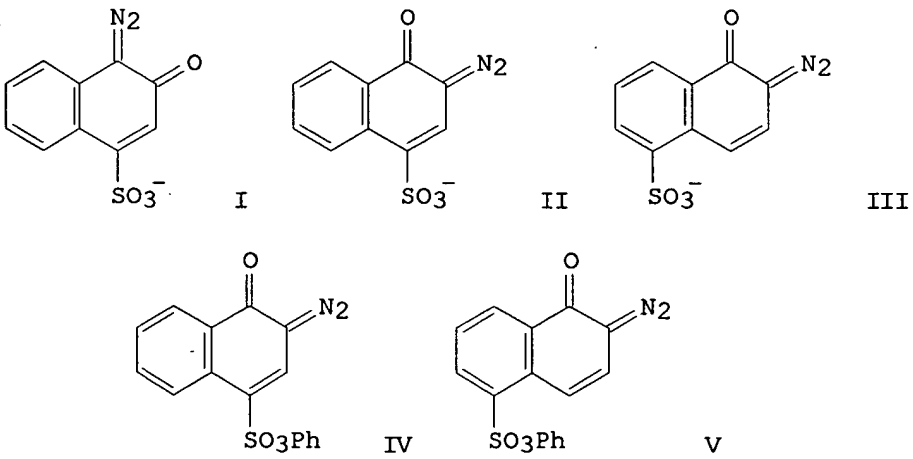
RN 153470-53-2 CAPLUS
CN Methanediol, 1H-inden-1-ylidene-, ion(1-) (9CI) (CA INDEX NAME)



RN 153470-55-4 CAPLUS
CN Methanediol, 1H-inden-1-ylidene-, ion(2-) (9CI) (CA INDEX NAME)



L11 ANSWER 7 OF 21 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1994:76751 CAPLUS
DOCUMENT NUMBER: 120:76751
TITLE: Flash photolytic generation and study of ketene and carboxylic acid enol intermediates formed by the photolysis of diazonaphthoquinones in aqueous solution
AUTHOR(S): Andraos, J.; Chiang, Y.; Huang, C. G.; Kresge, A. J.; Scaiano, J. C.
CORPORATE SOURCE: Dep. Chem., Univ. Ottawa, Ottawa, ON, K1N 6N5, Can.
SOURCE: Journal of the American Chemical Society (**1993**), 115(23), 10605-10
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: English
GI

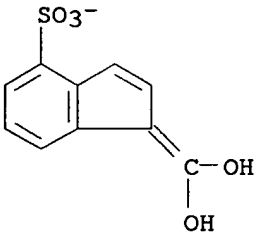


AB Flash photolysis of each of five diazonaphthoquinones (1-diazo-2(1H)-oxonaphthalene-4-sulfonate (I), 2-diazo-1(2H)-oxonaphthalene-4-sulfonate (II), 2-diazo-1(2H)-oxonaphthalene-5-sulfonate (III), Ph 2-diazo-1(2H)-oxonaphthalen-4-sulfonate (IV), and Ph 2-diazo-1(2H)-oxonaphthalene-5-sulfonate) (V) in aqueous solution was found to produce two short-lived intermediates preceding the ultimate indenecarboxylic acid reaction products. Decay of the first of these intermediates is catalyzed weakly by hydroxide ion but not by dilute perchloric acid nor by acetic acid

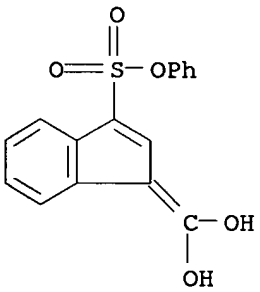
buffers, and its uncatalyzed reaction shows only weak solvent isotope effects; this serves to identify this intermediate as the ketene formed by photo-Wolff rearrangement of the diazonaphthoquinone. Decay of the second intermediate is catalyzed by perchloric acid in dilute acid solns., with saturation of this catalysis occurring in more concentrated acid, and it shows general acid catalysis in acetic acid buffers. The perchloric acid catalyzed reaction gives an appreciable solvent isotope effect in the normal direction (kH/kD > 1), which increases in magnitude as this catalysis becomes saturated This serves to identify this intermediate as the indenecarboxylic acid enol formed by hydration of the first intermediate. The form of acid catalysis by perchloric acid and the change in isotope effect indicates that this enol ketonizes through its enolate ion, with a shift of initial state from enol to enolate as the acidity of the medium is decreased; anal. of the kinetic data shows the enols to be rather strong acids, with pKa = 0.4-1.3.

IT **116670-10-1 145074-71-1 145074-72-2 152339-95-2**
RL: PRP (Properties)
(intermediate, photo-Wolff rearrangement of diazonaphthoquinones, polymerization of)

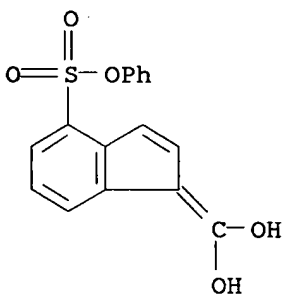
RN 116670-10-1 CAPLUS
CN 1H-Indene-4-sulfonic acid, 1-(dihydroxymethylene)-, ion(1-) (9CI) (CA INDEX NAME)



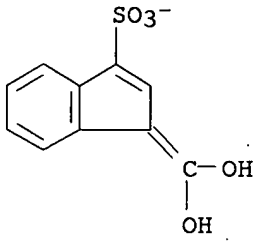
RN 145074-71-1 CAPLUS
CN 1H-Indene-3-sulfonic acid, 1-(dihydroxymethylene)-, phenyl ester (9CI) (CA INDEX NAME)



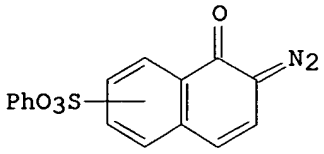
RN 145074-72-2 CAPLUS
CN 1H-Indene-4-sulfonic acid, 1-(dihydroxymethylene)-, phenyl ester (9CI) (CA INDEX NAME)



RN 152339-95-2 CAPLUS
CN 1H-Indene-3-sulfonic acid, 1-(dihydroxymethylene)-, ion(1-) (9CI) (CA INDEX NAME)



L11 ANSWER 8 OF 21 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1993:38553 CAPLUS
DOCUMENT NUMBER: 118:38553
TITLE: Synthesis and photochemistry of 1,2-naphthoquinonediazide-(2)-n-sulfonic acid derivatives
AUTHOR(S): Bendig, J.; Sauer, E.; Polz, K.; Schopf, G.
CORPORATE SOURCE: Inst. Org. Chem., Humboldt Univ., Berlin, 0-1040, Germany
SOURCE: Tetrahedron (**1992**), 48(42), 9207-16
CODEN: TETRAB; ISSN: 0040-4020
DOCUMENT TYPE: Journal
LANGUAGE: English
GI



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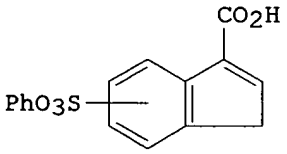
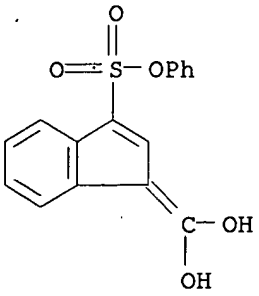


II

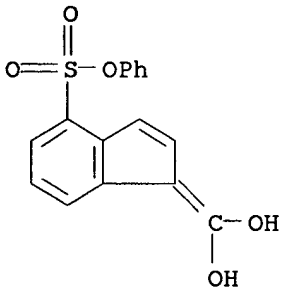
AB The 1,2-naphthoquinonediazide-(2)-6- and -7-sulfonic acid esters I (sulfonyl position = 7, 8) were synthesized for the first time starting from the corresponding 1-naphthylamine-6- and -7-sulfonic acids, resp., via Bucherer reaction, nitrosation, reduction, diazotation, sulfochlorination, esterification. The synthesis of the corresponding 8-sulfonic acid ester was not successful by this way. On photolysis, I form the corresponding (phenoxysulfonyl)indenecarboxylic acids II in the same manner like the known 5-sulfonic acid derivative On the other hand, photolysis of the 4-sulfonic acid ester photochem. induced ester cleavage occurs addnl. (λ <320 nm).

IT **145074-71-1P 145074-72-2P 145074-73-3P 145074-74-4P**
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and rearrangement of)

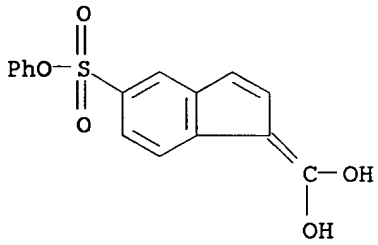
RN 145074-71-1 CAPLUS
CN 1H-Indene-3-sulfonic acid, 1-(dihydroxymethylene)-, phenyl ester (9CI) (CA INDEX NAME)



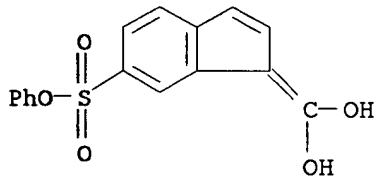
RN 145074-72-2 CAPLUS
CN 1H-Indene-4-sulfonic acid, 1-(dihydroxymethylene)-, phenyl ester (9CI) (CA INDEX NAME)



RN 145074-73-3 CAPLUS
CN 1H-Indene-5-sulfonic acid, 1-(dihydroxymethylene)-, phenyl ester (9CI) (CA INDEX NAME)



RN 145074-74-4 CAPLUS
CN 1H-Indene-6-sulfonic acid, 1-(dihydroxymethylene)-, phenyl ester (9CI) (CA INDEX NAME)



L11 ANSWER 9 OF 21 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1989:621868 CAPLUS
DOCUMENT NUMBER: 111:221868
TITLE: Photochemical reactions of 1-oxo-2-diazo-1,2-dihydronaphthalenes and reactivity of their products
AUTHOR(S): Tanigaki, K.; Honda, T.; Ebbesen, T. W.
CORPORATE SOURCE: Fundam. Res. Lab., NEC Corp., Kawasaki, 213, Japan
SOURCE: Polymeric Materials Science and Engineering (

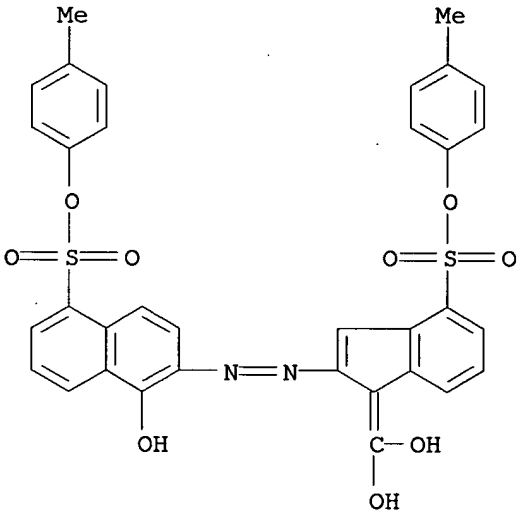
1989), 61, 291-5
CODEN: PMSEDG; ISSN: 0743-0515
DOCUMENT TYPE: Journal
LANGUAGE: English

AB Photochem. reactions of 4-tolyl 1-oxo-2-diazo-1,2-dihydronaphthalene-5-sulfonate (DNQ-5STL) were studied as a typical example of 6-membered ring α-diazoketones, together with its 2 prototype mols., i.e., 1-oxo-2-diazo-1,2-dihydrobenzene and 1-oxo-2-diazo-1,2-dihydronaphthalene, by reverse-phase liquid chromatog. The obtained products under different reaction conditions, such as photochem. reactions of pure solid DNQ-5STL in air and in vacuo, were examined The reactivity of the carboxy compds. produced in air or in a H2O-containing solution is discussed. They exhibit decarboxylation, dimerization or azo formation in the presence of bases, being markedly dependent on the type of mols. The azo formation rate constant of the 3-carboxyindene analog from DNQ-5STL is much greater than that of its dimerization.

IT **123658-18-4P**
RL: FORM (Formation, nonpreparative); PREP (Preparation)
(formation of, in reaction of photoproduct from photochem. reaction of tolyl oxodiazodihydronaphthalenesulfonate)

RN 123658-18-4 CAPLUS

CN 1-Naphthalenesulfonic acid, 6-[[1-(dihydroxymethylene)-4-[(4-methylphenoxy)sulfonyl]-1H-inden-2-yl]azo]-5-hydroxy-, 4-methylphenyl ester (9CI) (CA INDEX NAME)



L11 ANSWER 10 OF 21 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1988:601125 CAPLUS
DOCUMENT NUMBER: 109:201125
TITLE: Mechanism of photochemical conversion of 1,2-naphthoquinonediazides in solution
AUTHOR(S): Shibata, Tsuyoshi; Koseki, Kenichi; Yamaoka, Tsuguo; Yoshizawa, Masayuki; Uchiki, Hisao; Kobayashi, Takayoshi
CORPORATE SOURCE: Fac. Eng., Chiba Univ., Chiba, 260, Japan
SOURCE: Journal of Physical Chemistry (**1988**), 92(22), 6269-72
CODEN: JPCHAX; ISSN: 0022-3654
DOCUMENT TYPE: Journal
LANGUAGE: English

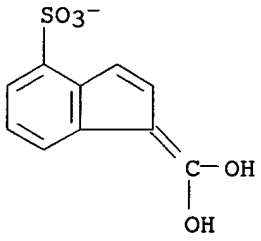
AB The photochem. conversion of 1,2-naphthoquinonediazide-5-sulfonic acid (NQDS) in solution was studied by nanosec time-resolved spectroscopy, and the observed transient absorption was assigned to the intermediate produced by the photodecompn. of NQDS. The intermediate was formed by the hydration of photochem. generated ketene. The formation rate constant of ketene hydrate in the mixed solvent of 1,4-dioxane/H2O increased with the H2O

concentration The conversion process from the ketene hydrate to 3-indenecarboxylic acid in aqueous solution is the acid-catalyzed reaction with a rate constant of 5.2 + 102 s-1 + 2.8 + 107 [H+] M-1 s-1, being H ion concentration

IT **116670-10-1P**
RL: FORM (Formation, nonpreparative); PREP (Preparation)
(formation of, in photolysis of naphthoquinonediazidesulfonate in aqueous solns.)

RN 116670-10-1 CAPLUS

CN 1H-Indene-4-sulfonic acid, 1-(dihydroxymethylene)-, ion(1-) (9CI) (CA INDEX NAME)



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S L1

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L6 STRUCTURE UPLOADED
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S L6

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L9 39 S L6 FULL

FILE 'CAPLUS' ENTERED AT 14:17:58 ON 14 NOV 2005
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L11 21 S L10 AND PY<2002

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L12 0 L11 AND L5

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L12 HAS NO ANSWERS
'IBIB ABS HITSTR ' IS NOT A VALID STRUCTURE FORMAT KEYWORD
Structure Formats
SIA ----- Structure Image, Attributes, and map table if it contains data. (Default)
SIM ----- Structure IMage.
SAT ----- Structure ATtributes and map table if it contains data.
SCT ----- Structure Connection Table and map table if it contains data.
SDA ----- All Structure DAta (image, attributes, connection table and map table if it contains data).
NOS ----- NO Structure data.
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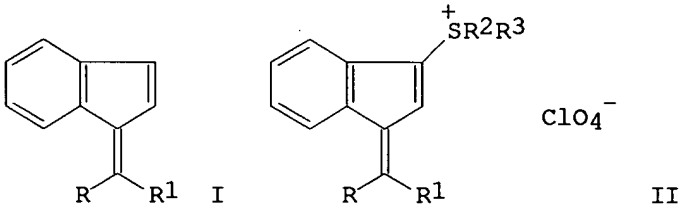
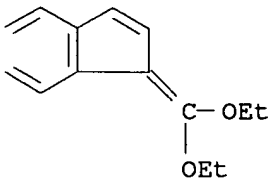
L11 ANSWER 11 OF 21 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1988:437562 CAPLUS
DOCUMENT NUMBER: 109:37562
TITLE: Electrophilic substitution of benzofulvenes with activated sulfoxides
AUTHOR(S): Teuber, Dorothee; Hartke, Klaus
CORPORATE SOURCE: Inst. Pharm. Chem., Univ. Marburg, Marburg, D-3550, Fed. Rep. Ger.
SOURCE: Liebigs Annalen der Chemie (**1988**), (1), 39-42
CODEN: LACHDL; ISSN: 0170-2041
DOCUMENT TYPE: Journal
LANGUAGE: German
OTHER SOURCE(S): CASREACT 109:37562
GI



AB The benzofulvenes I (R = R1 = Ph, Me, EtO, MeS; R = Me, R1 = Ph) were treated with R2R3SO [R2 = R3 = Me, PhCH2, Ph, p-MeC6H4; R2 = R3 = (CH2)4, CH2CH2OCH2CH2] in presence of (F3CCO)2O followed by aqueous LiClO4 to give the sulfoniobenzofulvene perchlorates II.

IT **115176-68-6P**
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and reaction with sulfoxides)

RN 115176-68-6 CAPLUS
CN 1H-Indene, 1-(diethoxymethylene)- (9CI) (CA INDEX NAME)

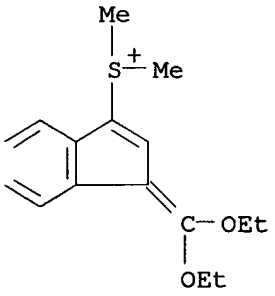


IT **115176-52-8P 115176-54-0P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)

RN 115176-52-8 CAPLUS
CN Sulfonium, [1-(diethoxymethylene)-1H-inden-3-yl]dimethyl-, perchlorate (9CI) (CA INDEX NAME)

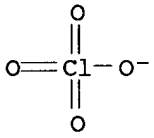
CM 1

CRN 115176-51-7
CMF C16 H21 O2 S



CM 2

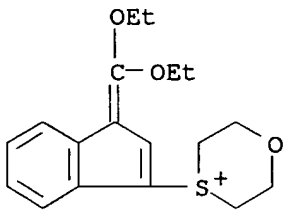
CRN 14797-73-0
CMF Cl O4



RN 115176-54-0 CAPLUS
CN 1,4-Oxathianium, 4-[1-(diethoxymethylene)-1H-inden-3-yl]-, perchlorate (9CI) (CA INDEX NAME)

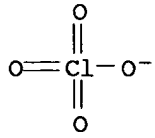
CM 1

CRN 115176-53-9
CMF C18 H23 O3 S



CM 2

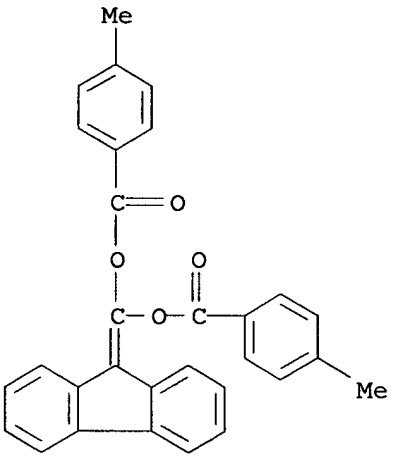
CRN 14797-73-0
CMF Cl O4



L11 ANSWER 12 OF 21 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1987:597239 CAPLUS
DOCUMENT NUMBER: 107:197239
TITLE: Nucleophilic attacks on carbon-carbon double bonds. 34. Intramolecular elements effect in competitive expulsion of two halide nucleofuges as a tool for investigating the rapid step of nucleophilic vinylic substitution
AUTHOR(S): Avramovitch, Bianca; Weyerstahl, Peter; Rappoport, Zvi
CORPORATE SOURCE: Dep. Org. Chem., Hebrew Univ., Jerusalem, 91904, Israel
SOURCE: Journal of the American Chemical Society (**1987**), 109(22), 6687-97
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: English

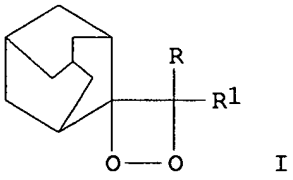
AB Substitution of 9-(bromochloromethylene)fluorene (I) and (p-O2NC6H4)2C:CClBr (II) with p-MeC6H4S- and p-MeC6H4O- ions gives the monobromo, monochloro, and disubstitution products. The [monochloro]/[monobromo] substitution product ratios were determined in CD3CN, DMSO-d6, and DMSO-d6-CD3OD under conditions where disubstitution was negligible. The ratios were 2.0-3.2, were slightly higher for I than for II, and showed no discernible solvent dependence. The ratios did not change in the presence of radical traps, although an ESR spectrum was observed with I and p-MeC6H4S-. The intermol. element effects kBr/kCl, derived from competitive substitution of I or II with their dibromo or dichloro analogs, were 1.2-1.76. The results were interpreted in terms of a multistep nucleophilic vinylic substitution via an intermediate carbanion, which may be formed either directly or by an initial single-electron transfer followed by combination of the anion radical with the radical. The product ratios were thus identified as the ratios of the rate consts. for Br- and Cl- expulsion [kel(Br)/kel(Cl) - the intramol. element effect] from the carbanion. The low ratios and their relative insensitivity to the solvent and to the delocalizing ability of neg. charge of the β-substituents were ascribed to an early transition state for halide-ion expulsion from the carbanion. Generalizations concerning the expulsion of poor and good nucleofuges from carbanions substituted by poor and good electron-withdrawing groups were discussed.

IT **110223-43-3P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)
RN 110223-43-3 CAPLUS
CN Benzoic acid, 4-methyl-, 9H-fluoren-9-ylidene[(4-methylbenzoyl)oxy]methyl ester (9CI) (CA INDEX NAME)



L11 ANSWER 13 OF 21 CAPLUS COPYRIGHT 2005 ACS on STN

ACCESSION NUMBER: 1983:160065 CAPLUS
DOCUMENT NUMBER: 98:160065
TITLE: Thermal stability of spiro[adamantane-[1,2]dioxetanes]
AUTHOR(S): Adam, Waldemar; Encarnacion, Luis A. Arias; Zinner, Klaus
CORPORATE SOURCE: Inst. Org. Chem., Univ. Wuerzburg, Wuerzburg, D-8700, Fed. Rep. Ger.
SOURCE: Chemische Berichte (**1983**), 116(3), 839-46
CODEN: CHBEAM; ISSN: 0009-2940
DOCUMENT TYPE: Journal
LANGUAGE: English
GI

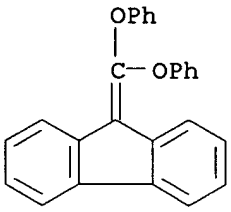


I

AB Activation parameters were determined for the thermolysis of I (R, R1 = Me, CH2Br; OPh, OPh; H, OCH2Ph; H, OC6H4Br-4; H, OPh) and some related 1,2-dioxetanes by a chemiluminescence method. The stabilization of I cannot be interpreted by inertial mass, torsional, or compression arguments. A transoid biradical, in which the participating orbitals are antiperiplanar, promotes C-C cleavage, but the bulky adamantane moiety hinders formation of this species from the initially formed cisoid biradical.

IT **85374-62-5**
RL: RCT (Reactant); RACT (Reactant or reagent)
(reaction of, with dibromodimethylhydantoin and hydrogen peroxide)

RN 85374-62-5 CAPLUS
CN 9H-Fluorene, 9-(diphenoxymethylene)- (9CI) (CA INDEX NAME)



L11 ANSWER 14 OF 21 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1977:55122 CAPLUS
DOCUMENT NUMBER: 86:55122
TITLE: Cyclic peroxides. 44. A convenient and efficient preparation of aromatic α-hydroperoxy acids via oxygenation of α-lithio enolates, prepared by direct α-lithiation of arylacetic acids
AUTHOR(S): Adam, Waldemar; Cueto, Omar
CORPORATE SOURCE: Dep. Chem., Univ. Puerto Rico, Rio Piedras, P. R.
SOURCE: Journal of Organic Chemistry (**1977**), 42(1), 38-40
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: English

AB Arylacetic acids were α-lithiated by treatment with BuLi in THF at -40°. The efficiency of the lithiation was shown by treatment of the α-lithiocarboxylic acids with electrophiles, i.e., D2O, Ph2CO, Me3SiCl, and O. In the last case, inverse addition at dry ice temperature gave the α-hydroperoxy acids corresponding to PhCH2CO2H, Ph2CHCO2H, and

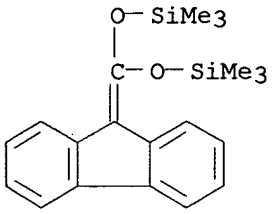
9-fluorenecarboxylic acid.

IT **40348-09-2P**

RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)

RN 40348-09-2 CAPLUS

CN 3,5-Dioxa-2,6-disilaheptane, 4-(9H-fluoren-9-ylidene)-2,2,6,6-tetramethyl- (9CI) (CA INDEX NAME)



L11 ANSWER 15 OF 21 CAPLUS COPYRIGHT 2005 ACS on STN

ACCESSION NUMBER: 1973:58504 CAPLUS

DOCUMENT NUMBER: 78:58504

TITLE: Ketene alkyltrialkylsilyl acetals. Synthesis, pyrolysis, and NMR studies

AUTHOR(S): Ainsworth, C.; Chen, Francis; Kuo, Yu-Neng

CORPORATE SOURCE: Dep. Chem., Colorado State Univ., Fort Collins, CO, USA

SOURCE: Journal of Organometallic Chemistry (**1972**), 46(1), 59-71
CODEN: JORCAI; ISSN: 0022-328X

DOCUMENT TYPE: Journal

LANGUAGE: English

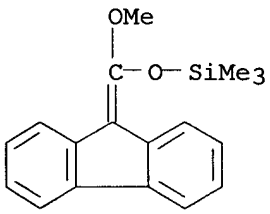
AB Ketene alkyltrialkylsilyl acetals RR1C:C(OMe)OSiMe3 (I) were prepared by reaction of disubstituted malonates and sodium-xylene, or by reaction of the α-anion of substituted acetates with Me3SiCl. Carbomethoxyketene methyltrimethylsilyl acetals Me2O2CRC:C(OMe)OSiMe3 (II) were also prepared Pyrolysis of diaryl I gave diaryl ketenes in good yield; the mechanism has been established as intramol. employing 18O. Alkyl, aryl and dialkyl I on pyrolysis gave ketene-ketene acetal addition compds. RR1C:C(OSiMe3)(CRR1CO2Me (III). Spectral studies of I are consistent with a dipolar structure Ar2C-C+(OMe)OSiMe3. Freedom of rotation about a carbon-carbon double bond is determined by the substituents. Spectral studies support fluxional behavior in II in which the carbomethoxy and trimethylsilyloxy groups are cis. The results of mass fragmentation of I are similar to their thermolytic cleavage. Interestingly, however, III in the mass spectrometer are fragmented into the ketene and ketene acetal fragments from which molecules they are thermally formed.

IT **40195-33-3**

RL: RCT (Reactant); RACT (Reactant or reagent)
(preparation pyrolysis and NMR of)

RN 40195-33-3 CAPLUS

CN Silane, (9H-fluoren-9-ylidenemethoxymethoxy)trimethyl- (9CI) (CA INDEX NAME)



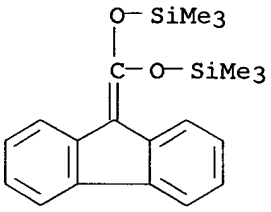
L11 ANSWER 16 OF 21 CAPLUS COPYRIGHT 2005 ACS on STN

ACCESSION NUMBER: 1973:43575 CAPLUS

DOCUMENT NUMBER: 78:43575
TITLE: Ketene bis(trialkylsilyl) acetals. Synthesis, pyrolysis, and spectral studies
AUTHOR(S): Ainsworth, C.; Kuo, Yu-Neng
CORPORATE SOURCE: Dep. Chem., Colorado State Univ., Fort Collins, CO, USA
SOURCE: Journal of Organometallic Chemistry (**1972**), 46(1), 73-87
CODEN: JORCAI; ISSN: 0022-328X
DOCUMENT TYPE: Journal
LANGUAGE: English

AB Two high yield synthetic methods are described for the preparation of alkyl, dialkyl, aryl and diaryl ketene bis(trialkylsilyl) acetals. One is by reaction of α-metalated trimethylsilyl carboxylates with Me3SiCl and the other is by interaction of dianions of carboxylic acids and Me3SiCl. The dianion of cyclopropane carboxylic acid and Me3SiCl gave C-silylated ester in 90% yield. Pyrolysis of diphenyl ketene bis(trialkylsilyl) acetals to diphenyl ketene and bis(trialkylsilyl) ethers was shown by crossover expts. to proceed intermol. pyrolysis of monosubstituted and dialkyl ketene bis(trimethylsilyl) acetals gave ketene-ketene acetal addition products (III) which on solvolysis afforded β-keto acids in high yield.

IT **40348-09-2**
RL: PRP (Properties)
(spectrum of)
RN 40348-09-2 CAPLUS
CN 3,5-Dioxa-2,6-disilaheptane, 4-(9H-fluoren-9-ylidene)-2,2,6,6-tetramethyl- (9CI) (CA INDEX NAME)



L11 ANSWER 17 OF 21 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1966:465536 CAPLUS
DOCUMENT NUMBER: 65:65536
ORIGINAL REFERENCE NO.: 65:12207d-h,12208a-h,12209a-b
TITLE: Carbocyclic substituted piperidyldioxolanes
INVENTOR(S): Hardie, Waldo R.; Halverstadt, Isaac F.
PATENT ASSIGNEE(S): Cutter Laboratories, Inc.
SOURCE: 15 pp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3262938		19660726	US	19610210 <--
PRIORITY APPLN. INFO.:			US	19610210

GI For diagram(s), see printed CA Issue.

AB The title compds. were prepared by the condensation of a ketone or ketal with a piperidyl vicinal glycol in the presence of HCl. The ketals were prepared by two methods: Method A, exchange between the appropriate ketone and 2,2-dimethoxypropane, and Method B, treatment of the ketone first with PCl5 then with NaOMe to form the dimethoxy derivative The tabulated R1R2C(OR)2 were prepared 2-Pyridyl-1,2-ethanediol-HCl was hydrogenated in H2O over PtO2 to give a mixture of 2 racemates of 2-piperidyl-1,2-ethanediol (I) HCl salt. Method, R1, R2, R, B.p./mm., n25D; A, Me, Ph, Bu, 75°/3, 1.4747; A, Et, Ph, Bu, 89-90°/3, 1.4767; A, PhCH2,

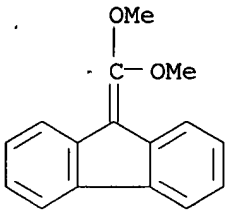
Bu, 147-54°/3, 1.5623; A, Ph, Ph, Me, m. 107-8°, -; A, Me, Ph2CH, Bu, 132-5°/1, 1.5620; A, Ph, PhCH2, Bu, 144-6°/3, -; B, 4-MeOC5H4, 4-MeOC6H4, Bu, 170-2°/1, 1.5302; B, 2-thienyl, Ph, Me, m. 56-9°, -; B, Ph, 4-ClC5H4, Me, 128°/1, 1.5667; B, 4-ClC6H4 4-ClC6H4, Me, m. 68.5-70°, -; B, fluoren-9-ylidene, Me, m. 86.7.5°, -; An alc. solution of this mixture was treated with NaOMe in MeOH to give the free bases which were dissolved in Et2O. The solution yielded the β racemate of I, m. 99-101°. After concentration, the mother liquors yielded the α-racemate of I, m. 77-8°. Acidic hydrolysis with HCl of 2,2-diphenyl-4-(2-piperidyl)-1,3-dioxolane (II) HCl salt α-racemate yielded I.HCl α-racemate, m. 100-1°, and hydrolysis of II.HCl β-racemate gave I.HCl β-racemate, m. 139-41°. Method C: I.HCl (86 g.), 103 g. (MeO)2CPh2, and 20 ml. iso-PrOH was heated at 130° with stirring. Dry HCl was passed in below the surface until the mixture was strongly acidic and the mixture was refluxed 8 hrs. with slow distillation of solvent which was replaced as needed. Removal of solvent followed by washing with Et2O and crystallization of the residue from EtOH then MeOHEt2O yielded 54.5 g. II.HCI, m. 248-52°. Extraction of the etherwashed residue from Method C with hot EtOH followed by filtration of the EtOH gave a residue, II.HCl β-racemate, m. 301°, and a solution which yielded II.HCl α-racemate, m. 256-60°. Method D: I.HCl (1436 g.) in 2 l. iso-PrOH was treated at 80° with 2012 g. (MeO)2CPH2 then with 1 g. dry HCl in iso-PrOH. The mixture was heated and stirred 2 hrs. to give 2042 g. crude II.HCl, m. 234-8°, containing approx. 60% α-racemate and 40% β-racemate of II.HCl. A II.HCl racemate mixture containing 15-20% β-racemate was converted to 76% DL-tartrate salt, m. 233-5°. II α-racemate DL-tartrate salt m. 222-8°. II.HCI α-racemate was also prepared directly from I α-racemate without isolation of the HCl salt. II.HCl α-racemate was converted to the free base then treated with L-(+)-tartaric acid to give (+)-II (+)-tartrate, m. 248-54° (decomposition). The mother liquors from this reaction were hydrolyzed to the free base then treated with D- (-)-tartaric acid to give (-)-II (-)-tartrate, m. 248-54° (decomposition). (+)-II (+)-tartrate was converted to the HCl salt, m. 248-54° (decomposition), α20D 34° (c 2, MeOH). Similarly prepared was (-)-II.HCl, m. 248-54°, α20D -34.5° (c 2, MeOH). I.HCl was condensed with EtCOPh in BuOH at 125° by Method C to give III (R1 = Et, R2 = Ph), m. 256-7°. Method E: I.HCl α-racemate (145.7 g.) and 209 g. EtC(OPr)2Ph in 900 ml. iso-PrOH was brought to pH 2 with anhydrous HCl gas then refluxed 1 hr. to give 175 g. III α-racemate (R1 = Et, R2 = Ph), m. 251.5-3°. After isolation of further α-racemate, the mother liquors were freed of α-racemate by successive formation of the free base, the DL-tartrate, the free base, and the HCl salt to give 2.4 g. of a γ-racemate of III.HCl (R1 = Et, R2 = Ph), m. 175-7°, solidified 195°, remelted at 241°. The following HI were prepared (method, starting racemate, R1, R2, and m.p. given): E, β, Et, Ph, 250-1°; D, mixture, H, Ph, 221°; E, β, Me, Ph, 241-3°; D, mixture,4-ClC6H4, Ph, 265-7°; D (no solvent), mixture, 4-ClC6H4, 4-ClC6H4, 210-15°; E, α, 2-thienyl, Ph, 221-3°; E, β, 2-thienyl, Ph, 282°; E, α, 4-MeOC6H4, 4-MeOC6H4, 282-3°; D, mixture, PhCH2, H, 163-5°; E, α, PhCH2, Ph, 240-4°; C (on ketone), mixture, PhCH2, PhCH2, 183-6°; E, α, PhCH2, PhCH2, 184-5°; E, β, PhCH2, PhCH2, 245°; E, β, PH2CH, Me, 205-10°; C (on ketone in BuOH), mixture, cyclohexyl, cyclohexyl, 243-5°; E, α, hexyl, hexyl (V), 153-5°; E, β, hexyl, hexyl (VI), 132-3°; E, α, octyl, octyl (VII), 105-12°; E, α, Bu, Bu (VIII), 160.5-62°. II β-racemate was hydrogenated at 60 psi. in glacial HOAc over Rh/Al2O3 to give III (R1 = R2 = cyclohexyl) β-racemate, m. 288°. II α-racemate with 37% aqueous HCHO was hydrogenated in MeOH over Pd/C to give IV (R = Me) α-racemate, m. 268-75°; methiodide m. 211-14°. Similarly prepared were: IV (R = Me)β-racemate, m. 183-5° (methiodide m. 237-8°); (+)-IV (R = Me), m. 275-87°, α25D 31.8° (c 1 MeOH); (-)-IV (R = Me), m. 283-7°, α24D -30.7° (c 1, MeOH). II.HCl α-racemate was converted to the

free base then treated directly with EtCOCl in (CH2Cl)2 at 0-5° to give IV (R = EtCO) α-racemate, m. 92-3.5°. Similarly prepared were: IV (R = ClCH2CO) α-racemate, m. 162.5-7.5°, its β-racemate, m. 153-4°, and IV (R = EtCO)β-racemate, m. 123-5°. Reduction of the latter with LiAlH4 in Et2O gave IV (R = Pr) β-racemate, m. 170-1.5°. Similarly prepared was IV (R = Pr) α-racemate, m. 201-2°. II α-racemate with PhCH2Br in C6H6 gave IV (R = PhCH2) α-racemate HCl salt, m. 172-4°. II β-racemate was refluxed 6 hrs. in absolute EtOH with PhCH2Br to give IV (R = PhCH2) β-racemate HCl salt, m. 212-15°: Similarly prepared were: (+)-IV (R = PhCH2) HCl salt (from the α-racemate), m. 201.5-203°, α25D 16.75° (c 2, MeOH); (-)-IV (R = PhCH2) HCl salt (from the α-racemate), m. 205-6°, α25D -16.62° (c 2, MeOH); (+)-IV (R = allyl) HCl salt (from the α-racemate), m. 198.5-9.5°, α22D 9.0° (c 1, MeOH). II α-racemate was heated 6 hrs. in a pressure bottle at 100° with (CH2)2O and MeOH-H2O 3:1 to give IV (R = HOCH2CH2) HCl salt α-racemate, m. 218-19.5°. IV (R = ClCH2CO)β-racemate was refluxed 3 hrs. with Et2NH in C6H6 to give IV (R = Et2NCH2CO)β-racemate, HCl salt m. 175-6°. Similarly prepared was the α-racemate, m. 182-3°. IV (R = Et2NCH2CO) β-racemate was reduced with LiAlH4 in Et2O to give IV (R = Et2NCH2CH2) β-racemate HCl salt, m. 180°. 4-Pyridylmethanol (IX) (100 g.) and 28 g. paraformaldehyde in 100 ml. H2O was treated with 2 ml. 10% NaOH, the mixture refluxed 20 hrs., then treated with 6N HCl to give a crystalline mixture of HCl salts of 4-pyridyl-1,2-ethanediol and IX. This mixture (122 g.) and 190 g. (MeO)2CPh2 in iso-PrOH and EtOH was acidified with HCl then refluxed 16 hrs. to give 27 g. 2,2-diphenyl-4-(4-pyridyl)-1,3-dioxolane-HCl (X), m. 211.514°. X was hydrogenated in EtOH. over PtO2 at 60 psi. to give 2,2-diphenyl-4-(4-piperidyl)-1,3-dioxolane-HCl (XI), m. 209.1-11.7°. Reductive methylation of XI gave 4-(1-methyl-4-piperidyl)-2,2-diphenyl-1,3-dioxolane-HCl (XII), m. 234.5-36°. Dry HCl gas was admitted under the surface of a solution of I.HCl (39 g.) and 40 g. cyclohexanone in 150 ml. iso-PrOH. After several days the mixture yielded 9.2 g. 2-(2-piperidyl)-1,4-dioxaspiro[4.5]decane-HCl (XIII, R = H), m. 223°. Other XIII prepared were (R, m.p. given): 6-Me, 247-50°; 6-Et, 263°; 7-Me, 232-3°; 8-Me, 258°; 7,9-di-Me, 219-20°; 8-tert-Bu, 264-5°; 6-Cl, 235-7°; 8-Cl (α-racemate), 239° (decomposed); 8-Cl (β-racemate), 206-7°; 8-Me-8-Ph, 215-30° (left to react 6 weeks at room temperature then the oily product was kept 5 months to crystallize); 8-Me-8-Ph (α-racemate), 244-52°; 8-Me-8-Ph (β-racemate), 202-19°; 8,8-di-Ph (β-racemate), 277-85°. Similarly prepared also was 2-(2-piperidyl)-1,4-dioxaspiro[4.6]undecane-HCl, m. 220-3°. Condensation of 9,9-dimethoxyfluorene (XIV) and I.HCl by Method D gave 4-(2-piperidyl)spiro(1,3-dioxolane 2,9'-fluorene) HCl salt (XV), decomposed 275°. Condensation of XIV with I α-racemate HCl salt by Method E gave XV α-racemate, m. 284-5°. Similarly prepared was XV β-racemate, m. 258-9°. IV (R = Me) β-racemate HCl salt was converted to the free base then to the N-oxide with H2O2 in MeOH; the HCl salt decomposed 200°. Similarly prepared were IV (R = Me) α-racemate N-oxide HCl salt, Me2CO solvate, m. 113°; and IV (R =PhCH2) α-racemate N-oxide HCl salt, m. 191° (decomposition). Reductive methylation of V gave 2,2-dihexyl-4-(1-methyl-2-piperidyl)-1,3-dioxolane-HCl α-racemate (XVI), m. 106°; methiodide m. 113-16°. The title compds. have antispasmodic and local anesthetic activity. (+)II is a central nervous depressant. V-VIII, XI, XII, and XVI have anti-pancreatic lipase activity.

IT **6861-54-7**, Fluorene, 9-carbonyl-, dimethyl acetal
(preparation of)

RN 6861-54-7 CAPLUS

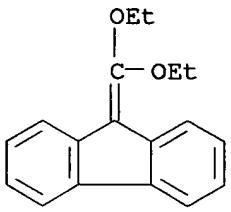
CN Fluorene, 9-carbonyl-, dimethyl acetal (7CI, 8CI) (CA INDEX NAME)



L11 ANSWER 18 OF 21 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1966:412000 CAPLUS
DOCUMENT NUMBER: 65:12000
ORIGINAL REFERENCE NO.: 65:2164f-g
TITLE: Acylation of aromatic hydrocarbons
AUTHOR(S): Shamis, E. M.; Dashevskii, M. M.
CORPORATE SOURCE: Polytech. Inst., Odessa
SOURCE: Zhurnal Obshchei Khimii (**1966**), 2(2), 280-2
CODEN: ZOKHA4; ISSN: 0044-460X
DOCUMENT TYPE: Journal
LANGUAGE: Russian

AB Aromatic substrates (0.1-0.2 mole) heated with RCOCl or PhSO2Cl (0.1 mole) in the presence of .apprx.0.3 + 10-3 mole AlCl3 6-10 hrs. at 140-50° (200° in some cases) gave the following acylated products in up to 92% yields: 2,4-Me2C6H3Bz, b9 178-81°; 2,4-isomer, b10 161°; 2,4-isomer, b. 320°; 2,4-Me2C6H3SO2Ph, m. 81-2°; p-BzC6H4OPh, m. 68°; p-MeOC6H4Bz, b8 180°, m. 61°; pMeOC6H4COAm, b8 156°, m. 41°; p-MeOC6H4COPr, b. 270-80°; Ph2SO2, m. 123°; p-MeC6H4Bz, m. 58°; mixed 1- and 2-C10H7COPh, b8 225°; p-BzC6H4Ph, b9 245°. Reactions with ZnCl2 were best for the more reactive aromatic substrates such as xylene, C10H8, Ph2, and MePh; AlBr3 gave poorer yields than AlCl3.

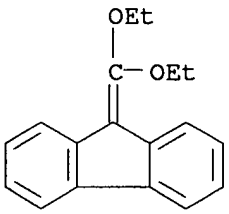
IT **6397-78-0**, Fluorene, 9-(diethoxymethylene)-
(preparation of)
RN 6397-78-0 CAPLUS
CN 9H-Fluorene, 9-(diethoxymethylene)- (9CI) (CA INDEX NAME)



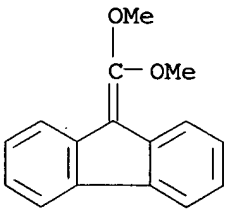
L11 ANSWER 19 OF 21 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1966:411999 CAPLUS
DOCUMENT NUMBER: 65:11999
ORIGINAL REFERENCE NO.: 65:2164e-f
TITLE: Synthesis of acetals by reaction of diazoalkanes with tert-butyl hypochlorite
AUTHOR(S): Baganz, H.; May, H. J.
CORPORATE SOURCE: Tech. Univ., Berlin
SOURCE: Angew. Chem., Intern. Ed. Engl. (**1966**), 5(4), 420
DOCUMENT TYPE: Journal
LANGUAGE: English

AB Diazoalkanes were converted by tert-BuOCl (I) in the presence of alcs. into the corresponding acetals. The appropriate diazo-alkane (0.2 mol) in dry Et2O and 100 cc. dry suitable alc. treated dropwise with stirring at -10° with 21.7 g. I yielded the corresponding RR'C(OR'')2 (R, R', R'', and % yield given): H, H, Et, 70; H, H, Pr, 76; H, H, (R'R'' =) CH2CH2, 57; Ph, H, Et, 49; Ph, Ph, Et, 43; (RR' =) 9-fluorenylidene, Et, 63.

IT **6397-78-0**, Fluorene, 9-carbonyl-, diethyl acetal
(preparation of)
RN 6397-78-0 CAPLUS
CN 9H-Fluorene, 9-(diethoxymethylene)- (9CI) (CA INDEX NAME)

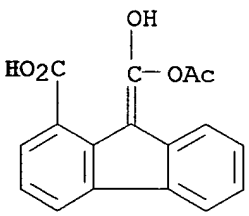


L11 ANSWER 20 OF 21 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1966:27475 CAPLUS
DOCUMENT NUMBER: 64:27475
ORIGINAL REFERENCE NO.: 64:5060h,5061a
TITLE: 4-(2-Piperidyl)-1,3-dioxolanes with local anesthetic, spasmolytic, and central nervous system activity
AUTHOR(S): Hardie, W. R.; Hidalgo, J.; Halverstadt, I. F.; Allen, R. E.
CORPORATE SOURCE: Cutter Lab., Berkeley, CA
SOURCE: Journal of Medicinal Chemistry (**1966**), 9(1), 127-36
CODEN: JMCMAR; ISSN: 0022-2623
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 64:27475
AB A series of 2-(2-piperidyl)-1,4-dioxaspiro[4.5]decanes and 4-(2-piperidyl)-1,3-dioxolanes with alkyl and aryl substituents was synthesized by the acid-catalyzed condensation of (2-piperidyl)-1,2-ethanediol with ketones and acetals. The yields were best when using acetals. Local anesthetic properties, generally with parallel papaverine-like activity, were widely distributed through the series and were most prominent when benzyl substituents were at the 2-position of the dioxolane ring. Several compounds had the unique property of shortening reaction time in the hotplate test. The spectrum of activities of one compound, 2,2-diphenyl-4-(2-piperidyl)-1,3-dioxolane, led to the separation of its racemates and the resolution of one of them.
IT **6861-54-7**, Fluorene, 9-carbonyl-, dimethyl acetal
(preparation of)
RN 6861-54-7 CAPLUS
CN Fluorene, 9-carbonyl-, dimethyl acetal (7CI, 8CI) (CA INDEX NAME)



L11 ANSWER 21 OF 21 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1961:76032 CAPLUS
DOCUMENT NUMBER: 55:76032
ORIGINAL REFERENCE NO.: 55:14399d-i,14400a-b
TITLE: The stereochemistry of aromatic compounds. XI. Experiments for the preparation of the anhydride of 1,9-fluorenedicarboxylic acid
AUTHOR(S): Kuhn, Richard; Breyer, Ursula
CORPORATE SOURCE: Max-Planck-Inst. Med. Forschung, Heidelberg, Germany

SOURCE: Chemische Berichte (**1961**), 94, 745-51
CODEN: CHBEAM; ISSN: 0009-2940
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
GI For diagram(s), see printed CA Issue.
AB cf. CA 49, 251i. Fluorene-1,9-dicarboxylic acid (I) could not form for steric reasons a normal anhydride which would have to be planar. I with Ac2O yielded the planar enol lactone II (R = Me) (III) and with AcCl the planar cyclic acylal II (R = AcO) (IV). IV with bases lost the Ac groups to give orange solns. containing apparently the enol salt of the planar anhydride II (R = OH) (V). I (1 g.) and 10 cc. Ac2O heated 2 hrs. at 150° yielded 720 mg. 1-methyl-3-oxo-2-oxa-2,3-dihydrofluoranthene (enol lactone of 9-acetylfluorene-1-carboxylic acid) (III), needles, m. 178-9° (EtOH); it sublimed without decomposition at 120°/0.0001 mm. III refluxed 0.5 hr. with 2N NaOH and acidified gave fluorene-1-carboxylic acid (VI), needles, m. 238°. III refluxed 2 hrs. with aqueous AcOH containing a little H_2SO_4 gave the 9-Ac derivative of VI, m. 205-10°. III with CrO_3 in AcOH yielded fluorenone-1-carboxylic acid (VII), m. 187-9°. I.0.5C6H6 (1 g.) refluxed about 2 hrs. with 15 cc. AcCl and evaporated, the residue dissolved in 25 cc. dry C6H6, treated with 50 cc. dry cyclohexane, and kept overnight at 0° gave 820 mg. IV, needles, m. 144-7° (C6H6-cyclohexane); it sublimed at 110°/0.0004 mm. with partial decomposition IV heated with aqueous alkali and acidified gave amorphous I, m. 232-9°. IV in C6H6 refluxed with excess PhNHNH2 gave the monophenylhydrazide of I, m. 260-4°; the filtrate concentrated yielded PhNHNHAc, m. 124° (C6H6). IV refluxed about 20 min. with MeOH yielded 100% 9-Me ester (VIII) of I, m. 213-16°. IV treated at room temperature with absolute MeOH turned yellow and developed with a half-time of 11 min. 2 new characteristic bands, one at 400-520 mμ and an intense, steep band at 322 mμ; the disappearance of the visible band occurred with a half-time of about 100 hrs.; the spectrum approached more and more that of VIII. IV with MeOH and 1 volume-% 0.1N NaOH gave an immediate yellow color. IV with MeOH and 1 volume-% 0.1N HCl remained colorless and developed a spectrum, similar to that of VIII, with a half-time of about 1 hr. IV with iso-PrOH developed with a half-time of 1.5 hrs. the characteristic bands; the further solvolysis was slower than in MeOH. IV with dioxane and 0.05 volume-% Et3N developed within a few min. the characteristic bands; the color decreased with a half-time of 2-3 hrs. I (500 mg.) in Me2CO treated with 400 mg. dicyclohexylcarbodiimide in C6H6, filtered from precipitated dicyclohexylurea, m. 213°, concentrated, dissolved in Et2O, and treated with CH2N2-Et2O gave only a non-crystalline product. 9-Carbomethoxyfluorene (IX) (2 g.) in 30 cc. Et2O treated with stirring under N with 0.3 cc. absolute MeOH and 400 mg. K, the mixture stirred over 2 hrs., and filtered, the unreacted K removed mech., and the filter residue treated dropwise in Et2O with AcCl in Et2O, filtered, and evaporated gave 500 mg. 9-Ac derivative of IX, m. 97° (cyclohexane). The infrared spectra of III and IV and the ultraviolet absorption spectrum of IV after 1.5 hrs. in MeOH were recorded.
IT **860215-12-9**, Fluorene-1-carboxylic acid, 9-(dihydroxymethylene)-, acetate
(preparation of)
RN 860215-12-9 CAPLUS
CN Fluorene-1-carboxylic acid, 9-(dihydroxymethylene)-, acetate (6CI) (CA INDEX NAME)



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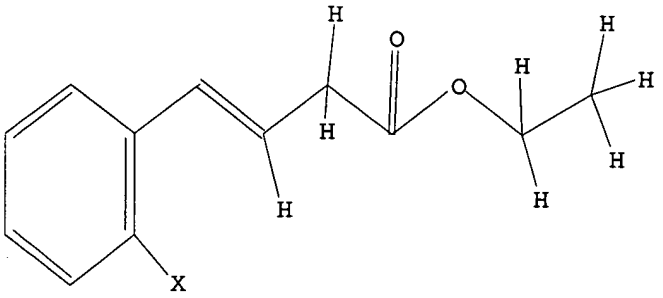
L1 HAS NO ANSWERS
L1 STR



Structure attributes must be viewed using STN Express query preparation.

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Use DISPLAY HITSTR (or FHITSTR) to directly view retrieved structures.

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SAMPLE SCREEN SEARCH COMPLETED - 39 TO ITERATE

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SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE **COMPLETE**
BATCH **COMPLETE**
PROJECTED ITERATIONS: 406 TO 1154
PROJECTED ANSWERS: 0 TO 0

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L3 0 L2

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Substance data SEARCH and crossover from CAS REGISTRY in progress...
Use DISPLAY HITSTR (or FHITSTR) to directly view retrieved structures.

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100.0% PROCESSED 877 ITERATIONS 4 ANSWERS
SEARCH TIME: 00.00.01

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L5 4 L4

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L5 ANSWER 1 OF 4 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 2005:219834 CAPLUS
DOCUMENT NUMBER: 142:269572
TITLE: Cyclopenta[a]naphthalene derivatives for liquid crystal display
INVENTOR(S): Lietzau, Lars; Bremer, Matthias; Klasen-Memmer, Melanie
PATENT ASSIGNEE(S): Merck Patent GmbH, Germany
SOURCE: PCT Int. Appl., 146 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005021682	A1	20050310	WO 2004-EP8632	20040802
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
DE 102004037387	A1	20050317	DE 2004-102004037387	20040802
PRIORITY APPLN. INFO.:			DE 2003-10338711 A	20030822

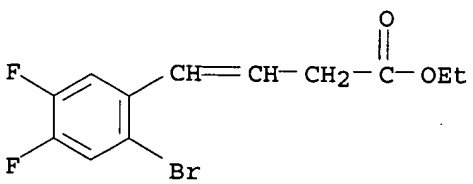
OTHER SOURCE(S): MARPAT 142:269572
GI

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB The invention relates to cyclopenta[a]naphthalene derivs. of general formulas I, II, III, IV or V (B = (fluoro-substituted) 5-membered ring; A = 1,4-phenylene, 1,4-cyclohexylene, etc.; Z = single bond, double bond, -CF2O-, -OCF2-, etc.; R = C1-15-alkyl, alkoxy, alkenyl, alkynyl; X1, X1a, X1b, X2, X3 = H, C1-15-alkyl, alkoxy, alkenyl, alkynyl; E1, E2 = H, C1-15-alkyl, alkoxy, alkenyl, alkynyl; n = 0-3), to the use thereof in liquid crystalline media, to liquid crystalline media containing at least one of said cyclopenta[a]naphthalene derivs., and to electro-optical display elements containing said liquid crystalline media. The synthesis examples are given.

IT **845832-82-8P**
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(synthesis of cyclopenta[a]naphthalene derivs. suitable for liquid crystal display)

RN 845832-82-8 CAPLUS
CN 3-Butenoic acid, 4-(2-bromo-4,5-difluorophenyl)-, ethyl ester (9CI) (CA INDEX NAME)



REFERENCE COUNT: 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS

RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 2 OF 4 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 2004:203786 CAPLUS
DOCUMENT NUMBER: 140:243724
TITLE: Cyclopenta[b]naphthalene derivatives
INVENTOR(S): Lietzau, Lars; Bremer, Matthias; Klasen-Memmer, Melanie; Heckmeier, Michael
PATENT ASSIGNEE(S): Merck Patent G.m.b.H., Germany
SOURCE: PCT Int. Appl., 103 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2004020375	A1	20040311	WO 2003-EP8285	20030728
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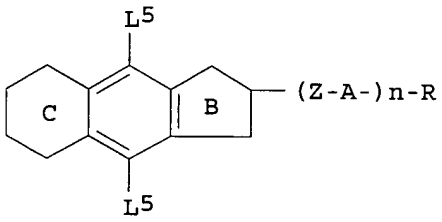
RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
DE 10238999	A1	20040304	DE 2002-10238999	20020826
DE 10324843	A1	20041223	DE 2003-10324843	20030602
EP 1532090	A1	20050525	EP 2003-790821	20030728
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, HU, SK				

PRIORITY APPLN. INFO.:
DE 2002-10238999 A 20020826
DE 2003-10324843 A 20030602
WO 2003-EP8285 W 20030728

OTHER SOURCE(S): MARPAT 140:243724
GI



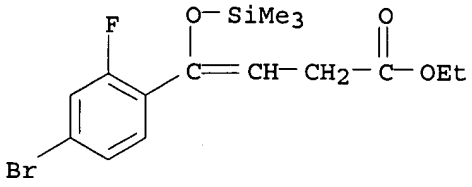
I

AB The invention relates to cyclopenta[b]naphthalene derivs. of general formula I (C =6-membered ring with substituents selected from H, C1-15-alkyl, alkoxy, etc.; B = 5-membered ring with substituents selected from H, C1-15-alkyl, alkoxy, etc.; Z = single bond, double bond, -CF2O-, -OCF2-, etc.; A = 1,4-phenylene, 1,4-cyclohexylene, etc.; R = H, C1-15-alkyl, alkoxy, etc.; L5, L6 = H, C1-15-alkyl, alkoxy, etc.; n = 0-3), the use thereof in liquid crystal or mesogenous media, liquid crystal or mesogenous media comprising at least one of said cyclopenta[b]naphthalene derivs. and electrooptical display elements comprising said liquid crystal or mesogenous media.

IT **669005-27-0P**
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation of cyclopenta[b]naphthalene derivs. suitable for liquid crystal display)

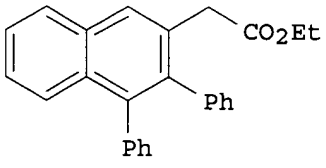
RN 669005-27-0 CAPLUS
CN 3-Butenoic acid, 4-(4-bromo-2-fluorophenyl)-4-[(trimethylsilyl)oxy]-,

ethyl ester (9CI) (CA INDEX NAME)



REFERENCE COUNT: 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 3 OF 4 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 2003:663938 CAPLUS
DOCUMENT NUMBER: 139:230561
TITLE: Synthesis of Substituted Naphthalenes and Carbazoles by the Palladium-Catalyzed Annulation of Internal Alkynes
AUTHOR(S): Huang, Qinhua; Larock, Richard C.
CORPORATE SOURCE: Department of Chemistry, Iowa State University, Ames, IA, 50011, USA
SOURCE: Journal of Organic Chemistry (2003), 68(19), 7342-7349
CODEN: JOCEAH; ISSN: 0022-3263
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 139:230561
GI



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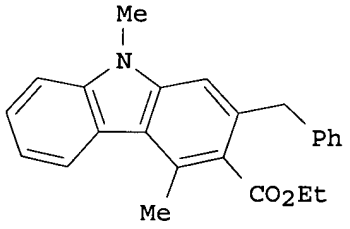


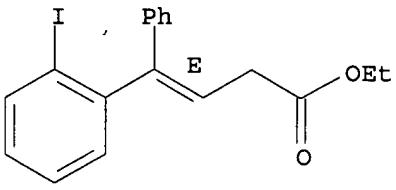
II

AB An efficient synthesis of highly substituted naphthalenes has been developed. The palladium-catalyzed annulation of internal alkynes, in which two new carbon-carbon bonds are formed in a single step, under relatively mild reaction conditions, is reported. This method has also been used to synthesize carbazoles, although a higher reaction temperature is required. The process involves arylpalladation of the alkyne, followed by intramol. Heck olefination and double-bond isomerization. This method accommodates a variety of functional groups and affords the anticipated highly substituted naphthalenes, e.g., I, and carbazoles, e.g., II, in good to excellent yields.

IT **593278-17-2P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(stereoselective preparation of Et (E)-(iodophenyl)butenoates via Wittig reaction of iodobenzophenone followed by hydrolysis, stereoselective Wittig reaction with (carboethoxymethylene)triphenylphosphorane, and double bond isomerization)

RN 593278-17-2 CAPLUS
CN 3-Butenoic acid, 4-(2-iodophenyl)-4-phenyl-, ethyl ester, (3E)- (9CI) (CA INDEX NAME)

Double bond geometry as shown.



REFERENCE COUNT: 53 THERE ARE 53 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

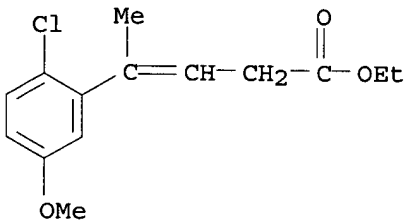
L5 ANSWER 4 OF 4 CAPLUS COPYRIGHT 2005 ACS on STN
ACCESSION NUMBER: 1959:111682 CAPLUS
DOCUMENT NUMBER: 53:111682
ORIGINAL REFERENCE NO.: 53:19988i,19989a-i,19990a-b
TITLE: Experiments on the synthesis of substances related to tetracyclines. IV. Preparation of 4-methyl-8-methoxy-1-naphthol and 1,8-dimethoxy-4-methyl-2-naphthoic acid, two useful intermediates for dedimethylaminotetrarubein synthesis
AUTHOR(S): Huang, Yao-Tseng; Tsung, Hui-Chuan; Tai, Li-Hsin; Sheng, Huai-Yu; Tu, Tung-Yuan
SOURCE: Huaxue Xuebao (1958), 24, 311-22
CODEN: HHHPA4; ISSN: 0567-7351
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
GI For diagram(s), see printed CA Issue.
AB cf. C.A. 53, 3171e. 1,8-(HO)2C10H6 (I) (2 g.) was methylated either by Staudinger's method (cf. S., et al., C.A. 15, 3445) to give 1.1 g. 8,1-MeOC10H6OH (II), m. 55°, soluble in hot dilute NaOH, and 0.2 g. 1,8-(MeO)2 C10H6, m. 157-9°, or by refluxing 5 hrs. I (40 g.), 33 g. MeI, and 40 g. anhydrous K2CO3 in 160 ml. Me2CO to give 25.8 g. II. Dry HCl was passed to a mixture of 8.5 g. II, 9 g. freshly prepared Zn(CN)2, and 1.3 g. KCl in 150 ml. Et2O with constant agitation at room temperature for 3 more hrs. beyond saturation and 150 ml. 50% EtOH was added to dissolve the separated solid and to yield on cooling 4.9 g. 4,5,1-HO(MeO)C10H5CHO (III), m. 112.5-13°; semicarbazone m. 244°. By refluxing 2 g. III and 6 g. Zn-Hg 4 hrs. in 15 ml. EtOH and 70 ml. MePh with 14 ml. concentrated HCl dropped in continuously 0.28 g. 4,8,1-Me(MeO)C10H5OH (IV) was obtained, m. 75-6° (MeOH). IV could also be prepared from III by Kishner-Wolff method modified by Huang-Minlon. Bromination of 7 g. IV with 5.94 g. Br in CCl4 at 70° 2.5 hrs. gave 9.28 g. 2,4,8,1-BrMe(MeO)C10H4OH (V), m. 104-5.5° (90% MeOH), which (2.73 g.) was methylated with Me2SO4 in 5% KOH-EtOH solution to yield 1.84 g. 2,4,1,8-BrMeC10H4(OMe)2 (VI), b3 168-78°, m. 44-6° (petr. ether). VI (750 mg.) in 5 ml. absolute Et2O was stirred with freshly prepared BuLi at -20° 10 min., CO2 was passed in, and the mixture was finally acidified with 6N HCl to give 0.37 g. 4,1,8,2-Me(MeO)2C10H4CO2H (VII), m. 121-2.5° (CCl4); the acid chloride m. 167.5-8.5°. In order to ascertain the structures of IV and VII another route to synthesize these compds. was proposed. 2,5-Cl(H2N)C6H3CO2H.HCl (50 g.) in 250 ml. 10% AcOH was diazotized with 15 g. NaNO2 in 125 ml. H2O at 0-5°, kept 1 hr., and boiled with 1.5 l. water to give 20.5 g. 2,5-Cl(HO)C6H3CO2H (VIII), m. 173-6° (3:10 Et2O-petr. ether). Methylation of 34.5 g. VIII in 100 ml. MeOH and 20 g. NaOH with 47 ml. Me2SO4 added dropwise and 28 ml. 50% KOH added at intervals to keep, the solution finally alkaline yielded 76.5% 2,5-Cl(MeO)C6H3CO2H, m. 172-3°, which (60 g.) was converted to 94% 2,5-Cl(MeO)C6H3COCl (IX), b5 126-8°, m. 24-5°, by heating to 70° with 67 g. PCl5. Addition of 18.3 g. IX in 10 ml. Et2O to an ether solution of 0.69 g. CH2N2 at 0° and keeping at room temperature 2 hrs. gave 2,5-Cl(MeO)C6H3COCHN2, m. 46-7° (ether-petr. ether), from which 2,5-Cl(MeO)C6H3COCH2Cl (X) (95% yield), m. 40°, or 2,5-Cl(MeO)C6H3COCH2Br (Xa) (95% yield), m., 14° was obtained by reaction with HCl or HBr, resp., in ether solution at 0° and room temperature 1 hr. Refluxing 2 g. X in 8 ml. C6H6 with CHNa(CO2Et)2 [solution of 0.21 g. Na, 20 ml. C6H6 and 5 ml. CH2(CO2Et)2] 24 hrs. and hydrolyzing the residue with KOH-MeOH (3.2 g. in 32 ml.) at refluxing temperature 3 hrs. gave 57% 2,5-Cl(MeO)C6H3COCH2CH(CO2H)2, m. 170° (Me2CO-C6H6)(decomposition),

which decomposed at 180° to 82% 2,5-Cl(MeO)C6H3COCH2CH2CO2H (XI), m. 92-3° (C6H6). Grignard reaction of 8 g. XI in 150 ml. dry Et2O and 50 ml. C6H6 with MeMgCl (from 2 g. Mg) at room temperature 1 hr., at refluxing temperature 12 hrs. followed by decomposition with 60 ml. 2N HCl gave 86% 2,5-Cl(MeO)C6H3CMe.CH2.CH2.CO.O (XII), b0.03 133-4°. By refluxing 14.5 g. XII in 38 ml. dry C6H6 with 12.5 ml. SOCl2 90 min., keeping overnight with 102 ml. absolute EtOH, and heating at 180° 1 hr., 2,5-Cl(MeO)C6H3CMe:CHCH2CO2Et (XIII) was obtained in 86% yield, b0.02 120°. Hydrogenation of 14.5 g. XIII in 100 ml. AcOH with 450 mg. PtO2 at 30° until 1.46 l. H was absorbed, and hydrolysis of the product with 10 g. KOH in 12 ml. H2O and 70 ml. MeOH at boiling temperature 2 hrs. gave 77% 2,5-Cl(MeO)-C6H3CHMeCH2CH2CO2H, m. 82-3° (petr. ether), which (8.98 g.) cyclized to 91% 4-methyl-5-chloro-8-methoxy derivative of 1-tetralone (XIV), m. 76-7°, when 8.4 g. PCl5, 9 ml. SnCl4 (in 9 ml. C6H6), and 32 ml. ice-HCl were added in order to the C6H6 solution with agitation. Bromination of 200 mg. XIV in CHCl3 gave the 2-bromo derivative, m. 85-6° (MeOH-H2O), which (0.2 g.) lost HBr very readily by heating 3 min. with 0.42 g. morpholine to form 69% 4,5,8,1-MeCl(MeO)C10H4OH, m. 122-3°. This (222 mg.) was finally hydrogenated in 30 ml. EtOH in the presence of 1.5 g. Pd-SrCO3(2%) in 5 ml. 10% KOH to yield 70% IV. Bromination of 2.4 g. XIV with 2 moles Br (3.36 g.) in CHCl3 (105 ml.) and keeping overnight gave 80% 2,2-dibromo-4-methyl-5-chloro-8-methoxy derivative of 1-tetralone, m. 129-30° (MeOH-CHCl3), which was converted into 73% 1,8-dimethoxy-2-bromo-4-methyl-5-chloronaphthalene (XV), m. 87-8°, by refluxing with MeONa-MeOH and Me2SO4 added in portions alternately 6-7 times. Chlorination of 0.5 g. VI with 0.126 g. Cl in 8 ml. AcOH or of 100 mg. XV with 25 mg. Cl in 4.5 ml. AcOH at room temperature gave 2,4-dichloro-5-methyl-7-bromo-8-methoxy-1-naphthol, m. 155-7° (AcOH), λ 250, 322, 340, 355 mμ. Refluxing 560 mg. V with EtOK and Et2SO4 added in portions alternately yielded 2,4,8,1-BrMe(MeO)C10H4OEt, b0.07 133.5-8.0°, m. 56-7° (petr. ether), which was chlorinated in AcOH to 2,4-dichloro-5-methyl-7-bromo-8-ethoxy-1-naphthol, m. 117.5-18.5° (AcOH). Attempt to synthesize XI by the condensation of IX and EtO2CCNaAcCH2CO2Et (XVI) followed by hydrolysis was unsuccessful although 5 g. 3-MeOC6H4COCl and XVI (0.7 g. Na and 7 g. EtO2CCHAcCH2CO2Et) refluxed 2 hrs., shaken 20 hrs. with 0.6 l. 1.5% KOH, purified by isolation of the product as semicarbazone, m. 179- 80°, and hydrolyzed with 2N HCl 130° gave 3-MeOC6H4- COCH2CH2CO2H, m. 107-8.5°.

IT **107625-25-2**, 3-Pentenoic acid, 4-(2-chloro-5-methoxyphenyl)-, ethyl ester
(preparation of)

RN 107625-25-2 CAPLUS

CN 3-Pentenoic acid, 4-(2-chloro-5-methoxyphenyl)-, ethyl ester (6CI) (CA INDEX NAME)



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